

PATENT SPECIFICATION

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(54) METHOD OF COATING GLASS BOTTLES

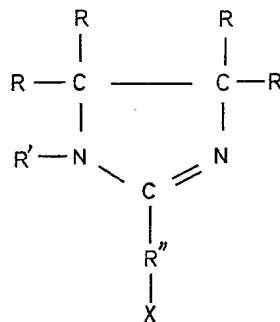
(71) We, VEBA-CHEMIE AKTIENGESELLSCHAFT, a German Body Corporate, of 466 Gelsenkirchen-Buer, 4690 Herne 2, Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of coating glass bottles, in particular with a transparent protective coating of a thermoset plastics material.

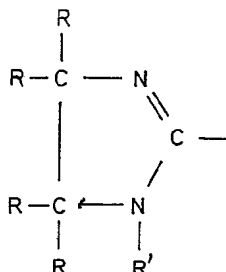
The coating of glass bottles with a firmly adhering uniform, transparent coat of plastics material makes glass bottles much safer for use as containers for beverages containing carbon dioxide, such as mineral water, beer, fruit juice beverages, and the like, and also lengthens the life of the bottles. As a result of the action of shocks and impacts, or by heating in sunlight or other sources of heat, unprotected bottles can sometimes explode and cause serious physical injuries, particularly eye injuries, to human beings.

Some coatings previously known for coating bottles have the disadvantage that the coating becomes cloudy when repeatedly cleaned, this possibly being due to an effect of recrystallisation of the plastics material when thermoplastics materials are used. Bottles of this kind give rise to an adverse optical impression and are therefore undesirable from the point of view of sales psychology.

According to the present invention, there is provided a method of coating a glass bottle with a transparent protective coating of a thermoset plastics material, the method comprising treating a clean glass bottle with an aqueous or alcoholic silane size; optionally, drying the bottle; heating the bottle at a temperature of from 180 to 250°C; applying a coating in the form of a powder composition to the heated bottle, the powder coating composition comprising a 1,2-epoxide containing on average at least one 1,2-epoxy group per molecule and having a "lower melting point" (as hereinafter defined) of more than 40°C and, as hardener, 4 to 12% by weight, based on the total weight of the powder coating, of an amidine of the general formula:—



wherein R is a hydrogen atom, an alkyl or aryl radical, R' is a cycloalkyl, hetero-cycloalkyl, or R radical, R'' is an alkylene or arylene radical or an alkyl- or aryl-substituted alkylene or arylene radical and X represents a hydrogen atom or a radical of formula:—



and then, only if the powder has not cured sufficiently, heating the coated bottles to cure the powder coating composition.

The protective layer applied in this manner is highly elastic and has excellent adhesion, so that if the glass should break or the bottle burst the splinters of glass cannot penetrate to the outside. After the destruction of the glass bottle the shape of the bottle is fully retained. The released kinetic energy is taken up by the resultant stretching and heating of the plastics coating.

A particular advantage is the ability of the present coatings to withstand hot, alkali-containing washing liquids in which the bottles are cleaned before being filled with the beverage. This is particularly advantageous in the case of reusable bottles, which are subjected to intensive cleaning before each filling operation.

An advantage of the coating obtained according to the method of the present invention is that even after repeated washing in hot alkaline washing liquid the plastics coating is not softened and there is no loss of adhesion. Furthermore, no optical variations occur.

Glass bottles coated in this manner can be used as containers for beverages containing carbon dioxide without any danger of breaking or bursting.

When the bottles are of the reusable type, the life of a coated bottle is substantially longer than that of an unprotected bottle, which because of the movement cycles is heavily stressed or may easily be damaged superficially through the rubbing against one another of sharp edges and through washing operations in hot liquids.

In accordance with the present method a cleaned glass bottle is first treated with an aqueous or alcoholic silane size. For this treatment preferably silanes having radicals which can be allocated to two different types of function are used. These are firstly C_{1-4} alkoxy radicals, particularly methoxy and ethoxy radicals which react with OH groups of the glass surface, and secondly organic radicals having functional groups which are capable of reacting either with the 1,2-epoxy compounds (e.g. amino groups) or with the hardener (e.g. epoxy groups or glycidyl radicals). Examples of suitable silanes are γ -aminopropyltrimethoxysilane, γ -aminopropyltriethoxysilane, glycidyloxypropyltrimethoxysilane and, glycidyloxypropyltriethoxysilane. Mixtures having identical functional radicals may also be used, that is to say mixtures of such groups which are reactive with epoxy groups or those having groups reacting with the hardeners. The glass bottle may for example be treated by dipping or spraying with the sizing agent. Bottles treated in this manner can then be dried. The drying may also be effected during the step of heating the bottle at from 180 to 250°C, that is to say to a temperature such as occurs in the course of the cooling process in the production of bottles.

The powder coating compositions described below are applied to the heated glass bottles by known methods, for example by electrostatic powder spraying. They may also be applied by fluidised bed coating or electrostatic fluidised bed coating.

The powder coating composition, which generally fuses at around 100°C, begins to fuse and set immediately and this results in excellent transparent flow of the film.

If the existing thermal capacity of the bottles is not adequate for hardening, the supply of heat may also be continued after the application of the powder coating composition until complete cross-linking is achieved.

The coated glass bottle may be subjected to hardening by heating at a temperature of from 140 to 240°C, preferably from 180 to 200°C.

For the preparation of the finely divided mixtures which are to be used as the powder coating, there are used 1,2-epoxy compounds having at least one 1,2-epoxy group per molecule and a melting range having a lower limit which is a temperature greater than 40°C. Throughout this specification this lower limit is referred to as the "lower melting point".

Compounds which comply with these characteristics are polyepoxy compounds

which are solid at 40°C and below, such as higher molecular weight compounds (so-called solid resins), and compounds which are solid because of their symmetrical construction or the size of the carbon residues bonded to the 1,2-epoxy group, compounds which have been produced by reacting liquid 1,2-epoxy compounds having more than one epoxy group per molecule with primary or secondary amines in such an amount that the adduct still contains at least on average one 1,2-epoxy group per molecule (so-called adduct hardeners) are also suitable as the 1,2-epoxide compound.

The 1,2-epoxy compounds may be either saturated or unsaturated, and may be aliphatic, cycloaliphatic, aromatic, or heterocyclic. They may in addition contain substituents which do not cause undesired side-reactions under the mixing and reaction conditions. For example, such side-reactions are not caused by alkyl- or aryl-substituents, hydroxyl groups, or ether groupings. Suitable 1,2-epoxide compounds belong to the following classes of substances: epoxides of single or multiple unsaturated hydrocarbons, halogen-containing epoxides, epoxy ethers of mono- or polyhydric alcohols and phenols, epoxy esters of mono- or polybasic acids, and also N-containing epoxides.

Preferred solid resins are 1,2-epoxy compounds having more than one epoxy group in the molecule and whose epoxy equivalent weight is from 500 to 1000. Examples of suitable such resins are solid polymeric polyglycidyl polyethers of 2,2-bis - (4 - hydroxyphenyl) - propane, which are obtained for example by reacting 2,2-bis(4 - hydroxyphenyl) - propane with epichlorohydrin in molar ratios of from 1:1.9 to 1.2 (in the presence of an alkali metal hydroxide in an aqueous medium). Polymeric polyepoxides of this kind can also be obtained by reacting a polyglycidyl ether of 2,2-bis - (4 - hydroxyphenyl) - propane with less than the equimolar amount of dihydric phenol, preferably in the presence of a catalyst, such as a tertiary amine, tertiary phosphine, or a quaternary phosphonium salt. The polyepoxide may also be a solid epoxidised polyester, which is obtained for example by reacting a polyhydric alcohol and/or a polybasic carboxylic acid or its anhydride with a low-molecular polyepoxide. Examples of such polyepoxides of low molecular weight are the liquid diglycidyl ether of 2,2 - bis - (4 - hydroxyphenyl) - propane, diglycidyl phthalate, diglycidyl tetrahydrophthalate, diglycidyl hexahydrophthalate, diglycidyl adipate, diglycidyl maleate, and the 3,4 - epoxycyclohexylmethyl ester of 3,4 - epoxycyclohexane - carboxylic acid.

Mixtures of solid polyepoxides can also be used, for example a mixture of a polyepoxide whose melting point is from 120 to 160°C and a polyepoxide having a melting point from 60 to 80°C (melting point determined by Durran's mercury method). Suitable mixtures contain from 30 to 50 weight per cent of a solid polyglycidyl ether of 2,2 - bis - (4 - hydroxyphenyl) - propane having an epoxy - equivalent weight of from 1650 to 2050 and a melting point of from 120 to 160°C, and from 50 to 70 weight per cent of a solid polyglycidyl polyether of 2,2 - bis - (4 - hydroxyphenyl) - propane having an epoxy-equivalent weight of from 450 to 525 and a melting point of from 60 to 80°C. If high epoxy-functionality appears desirable, a preferred polyepoxide is the polyglycidyl ether of 1,1,2,2 - tetra - (4 - hydroxyphenyl)ethane.

Epoxidised polybutadienes can also be used for this purpose.

As previously mentioned, in addition to the so-called solid resins, adduct hardeners are also suitable for carrying out the method of the invention. Such solid adduct hardeners may for example consist of liquid polyepoxides of multiple unsaturated hydrocarbons, such as vinylcyclohexene and dicyclopentadiene, epoxyethers of polyhydric alcohols and phenols, and aliphatic, cycloaliphatic, and aromatic diamines. A prerequisite for the suitability of an adduct of this kind is that its "lower melting point" should be above 40°C.

Like the pure epoxy compounds, mixtures of such compounds, for example mixtures of mono- and poly-epoxides, may also be used in the method of the invention.

Examples of cyclic amidines, that is to say imidazoline derivatives, which are suitable for use in the method of the present invention are 2 - methylimidazoline, 2,4-dimethylimidazoline, 2 - ethylimidazoline, 2 - ethyl - 4 - methylimidazoline, 2-benzylimidazoline, 2 - phenylimidazoline, 2 - phenyl - 4 - methylimidazoline, 2 - (o-tolyl) - imidazoline, 2 - (p - tolyl) - imidazoline, 1,4 - tetramethylene - bis - imidazoline, 1,1,3 - trimethyl - 1,4 - tetramethylene - bis - imidazoline, 1,3,3 - trimethyl - 1,4 - tetramethylene - bis - imidazoline, 1,3,3 - trimethyl - 1,4 - tetramethylene - bis - imidazoline, 1,3,3 - trimethyl - 1,4 - tetramethylene - bis - 4 - methylimidazoline, 2 - (m - pyridyl) - imidazoline, 2 - (p - pyridyl) - imidazoline, 1,2 - phenylene - bis - imidazoline, 1,3-phenylene - bis - imidazoline, 1,4 - phenylene - bis - imidazoline and 1,4 - phenylene-bis - 4 - methylimidazoline. Mixtures of these imidazoline derivatives may also be used according to the invention. Of these imidazolines, 2 - phenyl - imidazoline is

preferred. These compounds may also be used as the sole hardeners or cross-linking agents for 1,2-epoxy compounds.

The imidazoline derivatives described above are used in amounts such that the powder coating composition contains from 4 to 12 weight per cent, preferably from 6 to 8 weight per cent, based on the total weight of the powder coating composition are introduced.

If desired, certain conventional processing additives may be included in the powder coating compositions. Examples of such additives are flow promoting agents which are included for the purpose of improving the flow properties of the coatings. These agents may be chemical compounds or mixtures of compounds of different chemical types, for example polymeric or monomeric compounds, acetals, such as polyvinylformal, polyvinylacetal, polyvinylbutyral, polyvinylacetobutyral, or di - 2-ethylhexyl - isobutyraldehyde - acetal, di - 2 - ethylhexyl - n - butyraldehyde - acetal, diethyl - 2 - ethylhexanal - acetal, di - n - butyl - 2 - ethyl - hexanal - acetal, di - isobutyl - 2 - ethylhexanalacetal and di - 2 - ethyl - hexyl - acetaldehyde - acetal, ethers, such as the polymeric polyethylene and polypropylene glycols, copolymers of n-butyl acrylate and vinyl isobutyl ether, ketone aldehyde condensation resins, solid silicone resins, or mixtures of zinc soaps, fatty acids, and aromatic carboxylic acids. Commercially available products, such as "Modaflow", are also suitable for this purpose. The chemical character of Modaflow is not disclosed to purchasers thereof. It is merely known that they are a complex, polymeric active liquids. Such flow-promoting agents may be contained in the powder coating composition in amounts of from 0.2 to 5.0 weight per cent, based to the total weight of the powder coating composition.

The amounts of other conventional additives and components of the powder coating composition such as dyes soluble in the 1,2-epoxy compounds, and stabilisers may vary widely in relation to the amount of 1,2-epoxy compound and hardener. The amounts will depend on the desired quality of the resultant coatings.

Before use the powder varnish constituents are intimately mixed at temperatures below the hardening temperatures, extruded, and then ground. For practical purposes, a particle size of $<100\text{ }\mu\text{m}$ is preferably aimed at, with the distribution of particle sizes having its maximum value in the shape of from 30 to 50 μm .

The thicknesses of the hardened coatings can be adjusted to from 50 to 250 μm , depending on the stresses to which the bottles will be subjected.

The method of the present invention will now be illustrated by the following Examples.

General description of the method employed

Clean, untoughened glass bottles were first coated with an aqueous or alcoholic solution of γ - amino - propyltriethoxy - silane (1.5 weight per cent) at room temperature, forming an approximately monomolecular layer, and then dried.

The 1,2 - epoxy compounds used, which have the special characteristics and in practice are generally known as epoxy resins, were mixed in the weight proportions indicated with the imidazoline derivatives acting both as cross-linking agent and as hardener and with the flow-promoting agent, extruded, and then ground. The particle size of the constituents of the powder were less than 100 μm . The frequency distribution of the particle size had its maximum in the range from 30 to 50 μm . These fine-grained mixtures were then applied to the preheated glass bottles by electrostatic powder spraying, the powder fusing as a result of the heat of the heated bottles. Further heating at the temperatures and for the times indicated was then performed to further harden the coating. The properties of the resulting coatings were subjected to the tests described below.

Example 1

2 - Phenyl - imidazoline was mixed and ground with the epoxy resin and with a small addition of flow-promoting agent in the following ratio to form a coating powder composition:

Composition of the coating powder

Solid epoxy resin based on an adduct of 2,2 - bis - (4 - hydroxyphenyl) - propane - (diane) and epichlorohydrin, which had been subjected to HCl splitting and then reacted with additional diane and which according to information from the manufacturer has an epoxide equivalent weight of from 900 to 1,000, which corresponds to an epoxide value of from 0.10 to 0.11, and with a melting range of from

	90 to 100°C	weight %	
	2-Phenyl-imidazoline	93.5	
	Flow-promoting agent which is obtainable commercially	6.0	
5	under the name "Modaflow"	0.5	

This formulation was applied to glass bottles at a temperature of 200°C and hardened for 5 minutes at 180°C. The following tests were made on the coated bottles:

10	a. Visual judgement	The surface had a smooth, bright appearance.	
	b. Thickness of coating	60—70 μ m.	10
	c. Bursting pressure	The bottles burst at an internal pressure of from 22 to 26 atmospheres gauge, with a fine splinter pattern. The plastics coating held the resulting splinters completely together.	
15	d. Test in the washing machine	The washing liquid used in the test consisted of a "Calgonite"* sodium hydroxide solution (0.25/2.5 weight %) and was allowed to act on the bottles for 5 minutes at 85°C. The total time of passage through the washing machine amounted to 30 minutes. After this treatment the plastics material showed no detrimental changes.	15
20			20

*Calgonite=bottle cleaning agent based on the sodium salt of a polyphosphate.

25	e. Testing in line simulator, bottle temperature 80°C	The bottles were first filled with water at a temperature of 80°C and then kept for 10 minutes in a water bath at a temperature of 80°C. The heated bottles were then tested for one minute in the line simulator. In the region of the body of the bottles no abrasion could be detected on the plastics coating after the test.	25
30	5×1 minute running time in line simulator	The test described above was repeated five times. No damage was found.	30
35	f. Impact test (splinter cohesion)	The impact test was carried out with an impact energy of 73 kg cm. In this test a steel ball having a diameter of 80 mm was dropped from a height of 350 mm on to the empty bottle lying horizontally at a guide angle of 120°. The bottles broke and were deformed by the blow, but remained complete without glass splinters passing to the outside.	35
40	g. For the purpose of judging the coating medium under shock load, the "Penetration test with electronic measurement recording" was carried out in accordance with DIN 53 373. The results of this test show the flexibility and strength of a plastics film produced according to the method of the present invention.		40
	The coating thicknesses of the films were between 115 and 138 μ m. The following test adjustments were used:		

45	Form of test piece	flat film	
	Machine	Dynatester	45
	Test Temperature	24°C	
	Relative air humidity	70%	
	Penetrating body	hemisphere	
50	Results of 10 tests:		
	Damaging force F_s	14.17 kp	50
	Damaging work W_s	2.67 kpcm	
	Penetration work W_{ges}	4.05 kpcm	
	Damage deformation L_s	5.08 mm	

Example 2

55	2 - phenyl - imidazoline was worked up with the epoxy resin indicated below and with a small addition of flow-promoting agent in the following ratio to form the coating powder:		55
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Composition of coating powder

		weight %	
	Solid epoxy resin (as Example 1)	93.5	
	2-phenyl-imidazoline	6.0	
5	Flow-promoting agent (as Example 1)	0.5	5

This formulation was applied to glass bottles which had been heated about 240°C at the moment when the powder was applied. No further external heating was effected.

The tests of the coated bottles were carried out as explained in Example 1, and the results shown in Example 1 were obtained.

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Example 3

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1,4 - tetramethylene - bis - imidazoline was worked up with the epoxy resin indicated below and with a small addition of flow-promoting agent in the following ratio to form the coating powder:

Composition of coating powder

15		weight %	15
	Solid epoxy resin (as in Example 1)	94.0	
	1,4-tetramethylene-bis-imidazoline	5.5	
	Flow-promoting agent (as Example 1)	0.5	

This formulation was applied to glass bottles which had been heated to 200°C. No further external heating was effected. The following tests were then carried out:

	a. Visual judgement	The surface had a bright, smooth appearance.	
	b. Thickness of coating	70—80 μ m.	
	c. Bursting pressure	The bottles burst at an internal pressure of from 20 to 24 atmospheres gauge with a fine splinter pattern. The plastics coating held the splinters together.	
25	d. Test in washing machine	The test was carried out as in Example 1d. After the time indicated, here again no adverse changes of the plastics material were found.	25
30	e. Test in Line Simulator Tests as in Example 1e	The plastics coating showed only small abrasion points. After a running time of 5 \times 1 minute, no further damage was found.	30
	f. Impact test (splinter cohesion), test as in Example 1	The bottles broke and were deformed by the blow, but remained complete.	

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Example 4

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2 - phenyl - 4 - methyl - imidazoline was worked up with the epoxy resin indicated below and with a small addition of flow-promoting agent in the following ratio to form the coating powder:

Composition of coating powder

40		weight %	40
	Solid epoxy resin (as Example 1)	94.5	
	2-phenyl-4-methyl-imidazolin	5.0	
	Flow-promoting agent (as Example 1)	0.5	

This formulation was applied to glass bottles at a temperature of 200°C. The coatings were then hardened for 10 minutes at 200°C and subjected to the following tests:

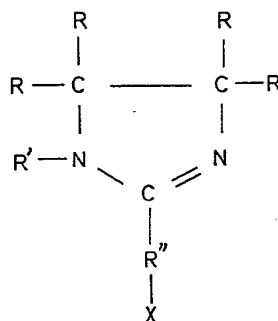
	a. Visual judgement	The surface had a bright, smooth appearance.	
	b. Thickness of coating	60—80 μ m.	
50	c. Bursting pressure	The bottles burst at an inside pressure of from 20 to 24 atmospheres gauge, with a fine splinter pattern. The plastics coating prevented splinters from penetrating to the outside.	50
	d. Test in washing machine	Test as in Example 1d. No adverse changes after the test period.	
55	e. Test in Line Simulator, Tests as in Example 1e	Apart from some light abrasion points, the coating remained intact. After a running time of 5 \times 1 minute, no further damage to the plastics coating was found.	55

- f. Impact test (splinter cohesion), test as in Example 1f The bottles broke and were deformed by the blow but remained complete.

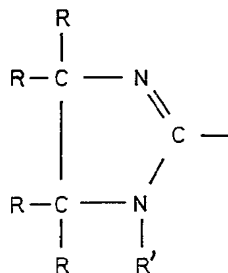
The words "Modaflow" and "Calgonite" used in this specification are registered Trade Marks.

WHAT WE CLAIM IS:—

1. A method of coating a glass bottle with a transparent protective coating of a thermoset plastics material, the method comprising treating a clean glass bottle with an aqueous or alcoholic silane size; optionally, drying the bottle; heating the bottle at a temperature of from 180 to 250°C; applying a coating in the form of a powder composition to the heated bottle, the powder coating composition comprising a 1,2-epoxide containing on average at least one 1,2-epoxy group per molecule and having a "lower melting point" (as hereinbefore defined) of more than 40°C and, as hardener, 4 to 12% by weight, based on the total weight of the powder coating, of an amidine of the general formula:—



wherein R is a hydrogen atom, an alkyl or aryl radical, R' is a cycloalkyl, heterocycloalkyl, or R radical, R'' is an alkylene or arylene radical or an alkyl- or aryl-substituted alkylene or arylene radical and X represents a hydrogen atom or a radical of formula:—



and then, only if the powder has not cured sufficiently, heating the coated bottles to cure the powder coating composition.

2. A method according to Claim 1, wherein the coated glass bottle is further subjected to hardening by heating at a temperature from 140 to 240°C.

3. A method according to Claim 2, wherein the hardening is carried out at a temperature of from 180 to 200°C.

4. A method according to any one of Claims 1 to 3, wherein the cyclic amidine used is 2-phenyl-imidazoline.

5. A method according to any one of the preceding claims, wherein the amount of cyclic amidine is from 6 to 8% by weight, based on the total weight of powder coating composition.

6. A method according to any one of the preceding claims, wherein at least one dye which is soluble in the 1,2-epoxy compound is added to the powder coating composition.

7. A method according to any one of the preceding claims, wherein the powder coating composition is applied by electrostatic spraying.

8. A method according to any one of Claims 1 to 6, wherein the powder coating composition is applied by fluidised bed coating or electrostatic fluidised bed coating.

9. A method for coating a glass bottle, substantially as hereinbefore described, with reference to any one of Examples 1 to 4.

5 10. A glass bottle having a transparent protective coating of thermoset plastics material when produced by a method as claimed in any one of Claims 1 to 9. 5

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